Radial Distributions Functions for Hydrogen-like Orbitals

by

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In this exercise you will explore some of the properties of the radial distribution functions of hydrogen-like one-electron orbitals. The radial distribution function is defined as \( r^2 \left( R_{n1}(r)\right)^2 \) where \( r \) is the distance from the nucleus (in units of Bohr radii \( a_o \)) and \( R_{n1}(r) \) is the radial wavefunction. Below are radial distribution functions for the 1s, 2s, 2p, 3s, 3p and 3d orbitals. The radial wavefunctions were taken from Pauling and Wilson, Introduction to Quantum Mechanics, McGraw-Hill, 1935.

\[
\text{raddis1s}[r_\text{, } z_\text{]} := r^2 (2 z^{1.5} \text{Exp}[-z r])^2
\]

\( r = \) distance from the nucleus in atomic units \( a_o = 52.91\text{pm} \).
\( z = \) nuclear charge

\[
\text{raddis2s}[r_\text{, } z_\text{]} := r^2 \left( \frac{1}{2} z^{1.5} \text{Exp}[2 z r/3] \right)^2
\]

\[
\text{raddis2p}[r_\text{, } z_\text{]} := r^2 \left( \frac{1}{6} z^{1.5} \text{Exp}[2 z r/3] \right)^2
\]

\[
\text{raddis3s}[r_\text{, } z_\text{]} := r^2 \left( \frac{1}{9} z^{1.5} \text{Exp}[2 z r/3] \right)^2
\]

\[
\text{raddis3p}[r_\text{, } z_\text{]} := r^2 \left( \frac{1}{9} z^{1.5} \text{Exp}[2 z r/3] \right)^2
\]

\[
\text{raddis3d}[r_\text{, } z_\text{]} := r^2 \left( \frac{1}{30} z^{1.5} \text{Exp}[2 z r/3] \right)^2
\]

The interpretation that we commonly place on the radial distribution function is that it represents the probability of finding the electron at a distance \( r \) from the nucleus, independent of angle (so it represents the probability of finding the electron on
the surface of a sphere of radius \( r \). This interpretation can be restated in terms of electron density to say that the radial distribution function represents the electron density on the surface of a sphere of radius \( r \). Given this interpretation, how would you interpret the value of the integral of the radial distribution function between \( r=0 \) and \( r=r' \)? In the integrals below, you can change the function being integrated and the nuclear charge, as well as the limits of integration. Play around with the integrals varying these parameters and describe how the results either support or refute your understanding of the radial distribution function. How can you verify that these are indeed probability functions?

\[
\begin{align*}
N\left[\text{Integrate}[r\text{addis1s}[r, 1], \{r, 0, 25\}]\right] &= 1. \\
N\left[\text{Integrate}[r\text{addis2p}[r, 1], \{r, 0, 25\}]\right] &= 1. \\
N\left[\text{Integrate}[r\text{addis3d}[r, 1], \{r, 0, 25\}]\right] &= 0.997421
\end{align*}
\]

Now prepare some plots of radial distribution functions for various orbitals. Use these plots to compare the relative sizes of orbitals and find internal radial nodes. Below is a sample plot for the 1s, 2s and 3s orbitals.

**Graph Setup**

```math
\$TextStyle = FontColor \rightarrow \text{RGBColor}[0, 0, 0]
FontColor \rightarrow \text{RGBColor}[0, 0, 0]

\text{plot1} = \text{Plot}[r\text{addis1s}[r, 1], \{r, 0, 25\}, \text{PlotStyle} \rightarrow \{\text{RGBColor}[1, 0, 0]\}, \\
\text{Frame} \rightarrow \text{True}, \text{PlotRange} \rightarrow \{0, 0.6\}, \text{DisplayFunction} \rightarrow \text{Identity}, \\
\text{FrameLabel} \rightarrow \{\text{"Sample plot of radial distribution functions"}, \\
\text{StyleForm}[\text{"raddis1s"}, \text{FontColor} \rightarrow \text{RGBColor}[1, 0, 0]], \\
\text{StyleForm}[\text{"raddis2s"}, \text{FontColor} \rightarrow \text{RGBColor}[0, 0, 1]], \\
\text{StyleForm}[\text{"raddis3s"}, \text{FontColor} \rightarrow \text{RGBColor}[0, 1, 0]]}\}; \\
\text{plot2} = \text{Plot}[r\text{addis2s}[r, 1], \{r, 0, 25\}, \text{PlotStyle} \rightarrow \{\text{RGBColor}[0, 0, 1]\}, \\
\text{DisplayFunction} \rightarrow \text{Identity}; \\
\text{plot3} = \text{Plot}[r\text{addis3s}[r, 1], \{r, 0, 25\}, \text{PlotStyle} \rightarrow \{\text{RGBColor}[0, 1, 0]\}, \\
\text{DisplayFunction} \rightarrow \text{Identity}
```

- Graphics -
Graph

Show[plot1, plot2, plot3, DisplayFunction → $DisplayFunction]

Sample plot of radial distribution functions

- Graphics -

To get at the concept of the "size" of an orbital find the distance you need to go from the nucleus to include 90-90% of the electron density

\[ r := \text{Range}[0, 10] \]

\[ \text{ed}[R_-, z_] = \int_0^R \text{raddis1s}[R, z] \, dR \]

\[ 1. + e^{-2Rz} (-1. + Rz (-2. - 2. Rz)) \]

\[ r \]

\{0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10\}

\[ \text{ed}[r, 1] \]

\{0., 0.323324, 0.761897, 0.938031, 0.986246, 0.997231, 0.999478, 0.999906, 0.999984, 0.999997, 1.\}

\[ r = . \]

Now differentiate the 1s function and solve for \( r \) at the minimum and maximum \( r^2 (2z^{1.5} e^{-zr}) \) by differentiation, yields

\[ 8 \, r \, z^{3.0} \, \text{Exp}[-zr]^2 - 8 \, r^2 \, z^{4.0} \, \text{Exp}[-zr]^2 \]

and has solutions(s)

\[ \left( \begin{array}{c} 0 \\ 1/z \end{array} \right) \]

\( r = 0 \) is the nucleus and \( r = 1/z \) (\( = 1 \) for \( z = 1 \)) is the maximum highest electron density or most probable distance if you use a particle model

Look at the effect of nuclear charge on the radial distribution function
Graph Setup

\[
\text{plot1} = \text{Plot}[r\text{addis1}[r, 1], \{r, 0, 10\}, \text{PlotStyle} \rightarrow \{\text{RGBColor}[1, 0, 0]\}, \\
\quad \text{Frame} \rightarrow \text{True}, \text{PlotRange} \rightarrow \{0, 1.5\}, \text{DisplayFunction} \rightarrow \text{Identity}, \\
\quad \text{FrameLabel} \rightarrow \{"r", \{\text{StyleForm["raddis1(r,1)", FontColor \rightarrow \text{RGBColor}[1, 0, 0]],[
\quad \text{StyleForm["raddis1(r,2)", FontColor \rightarrow \text{RGBColor}[0, 0, 1]]}\}}\}, \\
\quad \text{PlotLabel} \rightarrow \text{"effect of z on radial distribution"}]; \text{plot2} = \text{Plot}[r\text{addis1}[r, 2], \\
\quad \{r, 0, 10\}, \text{PlotStyle} \rightarrow \{\text{RGBColor}[0, 0, 1]\}, \text{DisplayFunction} \rightarrow \text{Identity}]
\]

- Graphics -

Graph

\[
\text{Show[plot1, plot2, DisplayFunction} \rightarrow \$\text{DisplayFunction}]
\]

- Graphics -

Do 2s and 2p have the same energy? It doesn't look like they are the same "size". The energy of an electron in an orbital is given by the expression

\[
E = -5 \int_0^{\text{large } r} \frac{r\text{addis2s}[r]}{r} \, dr
\]

For the case of 2s and 2p.

\[
\begin{align*}
E_{2s} &= N[-0.5 \text{Integrate}[r\text{addis2s}[r, 1]/r, \{r, 0, 25\}]] \\
&= -0.125 \\
E_{2p} &= N[-0.5 \text{Integrate}[r\text{addis2p}[r, 1]/r, \{r, 0, 25\}]] \\
&= -0.125
\end{align*}
\]

compare this to the energy of the 1s orbital
\begin{align*}
E_{1s} &= N[-0.5 \int r \text{addis1s}(r,1)/r, \{r,0,25\}] \\
&= -0.5
\end{align*}

These energies are in atomic units. Note that the result is consistent with the model that says that the energy of an orbital goes as $1/r^2$. It is also consistent with our convention that more stable energies are more negative.

The plot below shows that although the 2s orbital appears to extend further into space, the region closest to the nucleus is going to be most important in determining the energy.

**Graph Setup**

\begin{verbatim}
plot1 = Plot[raddis2s[r,1]/r, \{r,0,10\}, PlotStyle \rightarrow \{RGBColor[1,0,0]\},
Frame \rightarrow True, PlotRange \rightarrow \{0,0.1\}, DisplayFunction \rightarrow Identity,
FrameLabel \rightarrow \{"r",\{StyleForm[\text{\textfrac{raddis2s(r,1)}{r}}],\FontColor \rightarrow \{RGBColor[1,0,0]\},
StyleForm[\text{\textfrac{raddis2p(r,2)}{r}}],\FontColor \rightarrow \{RGBColor[0,0,1]\}\}\}];
plot2 = Plot[raddis2p[r,1]/r, \{r,0,10\}, PlotStyle \rightarrow \{RGBColor[0,0,1]\},
DisplayFunction \rightarrow Identity]
\end{verbatim}

**Graph**

\begin{verbatim}
Show[plot1, plot2, DisplayFunction \rightarrow $DisplayFunction]
\end{verbatim}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{graph.png}
\caption{Graph showing the 2s and 2p orbitals.}
\end{figure}

ClearAll[raddis1s, raddis2s, raddis2p, raddis3s, raddis3p, raddis3d, plot1, plot2, plot3, ed]

\begin{align*}
E_{2s} &= .; E_{2p} = .; E_{1s} = .
\end{align*}